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1 POLYURETHANE SELF-PRIMING TOPCOATS

5 STATEMENT OF GOVERNMENT INTEREST

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

10 CONTINUATION APPLICATIONS

This application is a Continuation-In-Part of copending application Serial Number 07/812,174 filed December 20, 1991. ~~This application~~ and a division of application ~~to~~ SN 07/936,983, filed 8-25-92.

BACKGROUND OF THE INVENTION

15 This invention relates to novel coating compositions and more specifically to corrosion-resisting coatings which can be applied directly to various surfaces particularly metal either as a high or low gloss, self-priming topcoat.

20 Various surfaces and particularly metal surfaces require the protection of coatings especially when the surfaces are exposed to a corrosive environment. Metal surfaces of aircraft, for example, are exposed to seawater which require protection from corrosion. Specifically, aircraft, e.g., Navy

1 aircraft, are exposed to seawater spray in addition to various  
acid-forming gases such as sulfur dioxide, carbon dioxide, etc.  
Moreover, in addition to aircraft, various machinery and  
equipment in the industrial environments, where fossil fuels  
5 are used need protection against corrosion. It is important  
therefore that the coating be resistant to corrosion, various  
chemicals, the weather and at the same time be flexible and  
have good adhesion to the substrates.

10 Presently, coating systems comprise one or more films,  
i.e., an undercoat, a sealant and a topcoat. Aircraft, for  
example, traditionally have been coated with high performance  
two-component protective films consisting of an epoxy primer  
and a polyurethane topcoat. The type of epoxy primers used on  
the aircraft are designed to adhere to the metal surface and  
15 help to improve the adhesion of the topcoat and together  
prevent corrosion of the metal. However, these undercoats  
require a topcoat, since the undercoats lack flexibility  
especially at low temperatures (-60°F) resulting in extensive  
cracking particularly in highly flexed areas of the aircraft.  
20 Moreover, the undercoats usually lack weather resistance and  
generally cannot be formulated in different colors required for  
aircraft.

25 In comparison, the polyurethane coatings of this  
invention, provides the necessary corrosion resistance, the  
required degree of flexibility, the desired optical properties,

1 and a resistance to weather and various chemicals. To obtain  
these characteristics, the multi-film coatings used heretofore  
generally required a dry-film thickness ranging up to about  
0.005 inches, e.g., up to about 10 mils or more which added  
5 considerable weight to the aircraft. In addition, the multi  
coats are time consuming to apply particularly since there is a  
drying time between each application. Further, the removal of  
a two-coat system can be difficult and time consuming and  
generates high levels of volatile organic (VOC) emissions  
10 during the operations.

In accordance with this invention the corrosion-resistant  
coating comprise a polyurethane binder derived from the  
reaction of at least one polyol, e.g., polyester polyol and an  
isocyanate, e.g., hexamethylene diisocyanate (HDI) or  
15 polyisocyanates in combination with a unique mixture of  
corrosion-inhibiting pigments consisting essentially of (1) an  
alkaline earth metal phosphate, e.g., zinc-barium phosphate,  
(2) zinc salts of benzoic acid or substituted benzoic acid, and  
(3) molybdate-modified zinc phosphates. All three of these  
20 compounds are essential, in the stated relative proportions, to  
provide a single high-gloss coating with the necessary  
corrosion resistance and adhesion characteristics required of a  
good top coat. In addition, titanium dioxide ( $\text{TiO}_2$ ) including  
spherical  $\text{TiO}_2$  particles, e.g., vesiculated beads of  $\text{TiO}_2$  are  
25 included as a pigment together with these three alkaline earth

1 metal or zinc salts. The coating compositions of this  
invention may be applied, as one coat, directly onto various  
hard surfaces such as metal and/or organic matrix composites,  
etc., and do not require an undercoat to provide a corrosion-  
5 resistant finish with desired optical and adhesion properties.

### SUMMARY OF THE INVENTION

A corrosion-resistant coating which can be applied  
directly to a surface as a self-priming topcoat comprising from  
about 20 to 60 parts by weight and preferably 30-50 parts of a  
10 polymeric urethane resin binder and a combination of three  
corrosion-resistant pigments consisting essentially of a  
molybdate-modified zinc phosphate, zinc salts of benzoic acid,  
and alkaline earth metal and/or zinc phosphates such as a  
complex zinc-barium phosphate, together with dispersing agents,  
15  $\text{TiO}_2$  pigments, and organic solvents

Accordingly, it is an object of this invention to provide  
a corrosion-resistant coating which can be applied directly to  
a surface e.g., metal, as a single coat.

20 It is another object of this invention to provide a  
coating which is flexible, resistant to corrosion, chemicals,  
and weathering, and has good adhesion characteristics.

It is still a further object of this invention to provide  
a coating for use on military or civilian aircraft of reduced

1 thickness to lower the weight thereon while at the same time  
providing the necessary corrosion resistance.

These and other objects of the invention are  
accomplished, in accordance with this invention, by providing a  
5 corrosion-resistant coating capable of being applied as a  
single coating with appropriate optical properties.

#### THE PREFERRED EMBODIMENTS

This invention is directed to a corrosion-resistant  
coating which functions as a primer and a topcoat. More  
10 specifically, this invention relates to a corrosion-resistant  
coating which comprises a major amount, e.g., 20 to 60 parts by  
weight of a urethane resin, i.e., polyurethane resin binders,  
and a minor amount of corrosion-inhibiting pigments, i.e.,  
alkaline earth metal compounds and/or zinc salts. The unique  
15 combination of pigments consist essentially of from about 5 to  
35 parts and preferably 10 to 30 parts by weight of an alkaline  
earth metal phosphate, e.g., zinc or zinc-barium phosphate, 0.5  
to 5 parts and preferably 1 to 3 parts by weight of a zinc salt  
of a benzoic acid or substituted benzoic acid, and about 5 to  
20 30 parts and preferably 10 to 25 parts by weight of a  
molybdate-modified zinc phosphate. In addition to the above  
metal compounds, depending on the opacity, etc., required of  
the coating, from 5.0 to 35 parts, and preferably from 5.0 to  
15 parts by weight of titanium dioxide pigment, based on the

1 total weight of the coating, is added as an additional pigment.  
Up to about 100% of the total amount of  $\text{TiO}_2$  may be in the form  
of vesiculated beads, e.g., from 0 to 50% of the  $\text{TiO}_2$  in the  
coating are beads. Generally, the coating is applied as a high  
5 solids organic solution and therefore generally contains from 0  
to 3.0 and preferably about 0.1 to 2.0 parts by weight of at  
least one oil soluble dispersing or wetting agent such as Anti-  
Terra-204 or BYK-320. Anti-Terra-204 is a carboxylic acid of  
polyamine-amides and BYK-320 is a polyether modified  
10 methylalkylpolysiloxane copolymers. Various other nonionic or  
anionic dispersing agents known as oil soluble dispersants or  
paint additives may be used in the coating. In addition, the  
coating contains from about 0 to 50 parts, e.g. as needed or  
from 10 to 25 parts by weight of the total coating of at least  
15 one organic solvent, e.g., Mil-T-81772 or various mixtures of  
paint solvents.

The organic binder of the coating comprises a  
polyurethane, and more particularly an aliphatic polyurethane  
derived from the reaction of a polyol and a multi-functional  
20 aliphatic polyisocyanate. The polyol is preferably used as a  
solution in an organic solvent e.g. toluene, xylene, n-butyl  
acetate, propylene glycol monomethyl ether acetate, methyl  
ethyl ketone, etc. The polyisocyanate is used as a 100% solid  
but also can be diluted with any of the above organic solvents.  
25 The hydroxyl number of the polyol, i.e., polyester polyols and

1 the isocyanate (NCO) content or the equivalent weights of the  
polyisocyanate and polyol are determined in order to obtain the  
desired polyurethane. The preferred polyols and  
polyisocyanates are reacted in approximately stoichiometric  
5 amounts so that the NCO to OH ratio ranges from about 0.85 to  
1.4 equivalent of the NCO to 1.0 equivalent of the OH, or at  
about a 1.0 to 1.0 ratio of the NCO to OH.

The combination of metal salts and/or pigments is unique  
and consists essentially of specific amounts of an alkaline  
10 earth metal phosphate, e.g., zinc phosphate or zinc-barium  
phosphate etc., zinc salts of benzoic acid or a substituted  
benzoic acid and a molybdate-modified zinc phosphate. These  
three metal salts or pigments used alone and in combination  
with  $TiO_2$  provide outstanding corrosion protection and enables  
15 the coating to be used as a self-priming high-gloss or low-  
gloss topcoat.

The particular alkaline earth metal complexes or zinc  
phosphates used in preparing the coating composition is  
preferably a zinc-barium phosphate. The preferred zinc salt of  
20 benzoic acid is specifically characterized as having at least  
one hydroxyl group and nitro ( $NO_2$ ) substituent and molecular  
weights of about 100 - 500, e.g. 300, density of about 2-3  
grams per milliliter and a specific surface area of  $16M^2$ /gram.  
The benzoic acid salts are commercial products obtained from  
25 BASF and identified as Sicorin-RZ.

The preferred zinc salts of the benzoic acids have at least one hydroxyl substituent and one (NO<sub>2</sub>) group. The zinc salt of the benzoic acids are further characterized as having molecular weights of approximately 100 to 500. The preferred zinc phosphates, are complex alkaline earth zinc phosphates, e.g., zinc-barium phosphate. This zinc phosphate is available as Phos-Plus (J0866) from Mineral Pigments Corporation. A preferred molybdate-modified zinc phosphate, i.e, HEUCOPHOS-ZMP from HEUCOTECH LTD. has the following analysis:

<u>Chemical Analysis</u>	<u>Percent</u>
Zinc content as Zn	55-57
Molybdate content as Mo O <sub>3</sub>	1.5
Phosphate content as PO <sub>4</sub>	38-41
Loss on ignition as 600°C	10-12
Water soluble Cl	<0.05
Water soluble SO <sub>4</sub>	<0.05
Water soluble Mo	0.1
pH	7

Other molybdate-modified zinc phosphates include the metal complexes or mixtures of an alkaline earth metal from Group II of the Periodic Table such as a zinc molybdate-zinc phosphate, and more specifically a barium or calcium-zinc molybdate/zinc phosphate, such as (CaMoO<sub>4</sub>, CaCO<sub>3</sub>, ZnO, Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>). These complex or mixed metal phosphates are available commercially as MOLY-WHITE from the Sherwin Williams Co. of Cleveland, Ohio.

In addition to utilizing the above combination of metal pigments in the required ratios, titanium dioxide is added to the coating to provide reinforcing strength and to add color,

1        hiding and opacity to the coating. Other additives that maybe  
used include tinting or coloring agents which may be added to  
the coating in small but effective amounts such as zinc oxide,  
antimony oxides, barium sulfate, calcium carbonate and one or  
5        more of the organic pigments such as the phthalocyanine colors  
e.g. greens or blues, etc.

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1 Specifically, the corrosion resistant coatings of this invention can be prepared by milling the ingredients set forth in the following Examples.

	<u>EXAMPLE 1</u>	<u>EXAMPLE 2</u>
5	<u>Ingredients</u>	<u>Parts by Weight</u> (Ranges)
	Polyurethane Resin or Binder derived from polyester polyols and polyisocyanates	30-50
	Titanium dioxide	5-15
	Titanium dioxide (vesiculated beads)	0.1-5.0
10	Alkaline earth metal phosphates and complexes such as zinc and/or barium phosphates	10-30
	Zinc salts of substituted benzoic acids	1-3
	Molybdate-modified Zinc Phosphates (e.g., MOLY WHITE-MZAP or HEUCOPHOS-ZMP)	10-25
15	Dispersing agents, e.g., Anti-Terra-204 (Oil Soluble Anionic or Nonionic dispersants)	0.1-2.0
	Organic solvents for coatings	0-50

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EXAMPLE 3IngredientsParts by Weight

	Polyurethane Resin derived from polyester polyol in organic solvents (i.e., propylene glycol monomethylether acetate, N-butyl acetate) and polyisocyanate	39.2
5	Titanium Dioxide Pigment	10.2
	Titanium Dioxide Vesiculated Beads	0.6
	Zinc-Barium Phosphate	24.5
	Zinc Salt of a substituted Benzoic Acid (Sicorin RZ)	2.4
	Molybdate-Modified Zinc Phosphate (HEUCOPHOS-ZMP)	22.7
10	Dispersant (BYK-320)	0.3
	Organic Solvents	As Needed

EXAMPLE 4IngredientsParts by Weight

15	Polyurethane Resin derived from 79% solids solution polyester polyol in organic solvents (propylene glycol monomethyl ether acetate, n-butyl acetate) and 100% solids of a polyisocyanate	49.8
	Titanium Dioxide Pigment	32.1
	Titanium Dioxide Vesiculated Beads	0.0
	Zinc-Barium Phosphate	6.4
	Zinc Salt of a substituted Benzoic Acid (Sicorin RZ)	0.6
20	Molybdate-modified Zinc Phosphate (HEUCOPHOS-ZMP)	10.6
	Dispersant (Anti-Terra-204)	0.3
	Organic Solvents	As Needed

EXAMPLE 5

Ingredients

Parts by Weight

1	Polyurethane Resin derived from 79% solids solution of polyester polyol in organic solvents (propylene glycol monomethyl ether acetate, n-butyl acetate) and 100% solids of a polyisocyanate	32.7
5	Titanium Dioxide Pigment	14.7
	Titanium Dioxide Vesiculated Beads	0.5
	Zinc-Barium Phosphate	22.8
	Zinc Salt of a substituted Benzoic Acid (Sicorin RZ)	2.2
	Molybdate-modified Zinc Phosphate (Heucophos ZMP)	26.9
10	Dispersant	0.3
	Organic Solvents	As Needed

EXAMPLE 6

Ingredients

Parts by Weight

15	Polyurethane Resin derived from 79% solids solution of polyester polyol in organic solvents (propylene glycol monomethyl ether acetate, n-butyl acetate) and 100% solids of a polyisocyanate	41.6
	Titanium Dioxide	14.1
	Titanium Dioxide Vesiculated Beads	1.4
	Zinc-Barium Phosphate	23.5
	Zinc Salt of a substituted Benzoic Acid (Sicorin RZ)	2.3
20	Molybdate-modified Zinc Phosphate (Heucophos ZMP)	16.8
	Dispersant	0.3
	Organic Solvents	As Needed

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EXAMPLES 7-10

		<u>% by Weight</u>			
<u>Ingredient</u>		<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
5	1. 79% solids solution polyester polyol in organic solvents (propylene glycol monomethyl ether acetate, n-butyl acetate)	27.4	34.2	23.0	28.9
	2. Titanium Dioxide Pigment	10.6	32.6	15.3	14.4
	3. Titanium Dioxide Vesiculated Beads	0.6	0.0	0.5	1.5
	4. Zinc-Barium Phosphate	25.4	6.4	23.7	24.1
	5. Zinc Salt of a substituted Benzoic Acid (Sicorin RZ)	2.5	0.6	2.3	2.4
10	6. Calcium-Zinc Molybdate/Zinc Phosphate (Moly-White MZAP)	20.1	9.5	24.0	14.7
	7. Dispersant (Anti-Terra-204)	0.3	0.3	0.3	0.3
	8. (100% Solids) Polyisocyanate Resin	13.1	16.4	11.0	13.8

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**EXAMPLES 11-14**

		<u>% by Weight</u>			
	<u>Ingredient</u>	<u>E</u>	<u>F</u>	<u>G</u>	<u>H</u>
	1. 79% solids solution polyester polyol in organic solvents (propylene glycol monomethyl ether acetate, n-butyl acetate)	25.7	33.2	21.3	27.5
5	2. Titanium Dioxide Pigment	9.9	31.6	14.1	13.8
	3. Titanium Dioxide Vesiculated Beads	0.6	0.0	0.5	1.4
	4. Zinc-Barium Phosphate	23.7	6.2	21.9	22.9
	5. Sicorin RZ	2.3	0.6	2.1	2.2
	6. Zinc Molybdate/Zinc Phosphate (Moly-White MZAP)	25.1	12.3	29.6	18.7
10	7. Dispersants (Anti-Terra-204/BYK-320)	0.3	0.3	0.3	0.3
	8. Polyisocyanate Resin (100% Solids)	12.3	15.8	10.2	13.1

In Examples 7-14, the polyester polyol blend was used as a solution, e.g., 79% solids in propylene glycol monomethyl ether acetate and butyl acetate. The polyisocyanate was 100% solids, e.g., substantially containing no solvents.

Preferably, the coatings are prepared by mixing all of the ingredients, except the polyisocyanate and then milling the mixture to a fineness of about 5 for camouflage and .7 for high gloss colors on the Hegman scale according to ASTM D1210. Subsequently, the polyisocyanate is added before the application of the coating to the substrate. The coating is

1 applied on the substrate at thickness ranging from about 0.001  
to 0.003 inches e.g. from 0.5 to about 10 mils and preferably  
1 to 3 mils. The coating may be applied by various methods  
including spraying, rolling, or brushing onto the surface  
5 depending on the viscosity. The viscosity of the coating for  
the particular application may be achieved by adjusting the  
content of the solvent within the ranges specified herein and  
by the selection of the particular reactants used to form the  
urethane resin. After the coating is applied to the surface,  
10 the solvent is evaporated at room or elevated temperatures and  
is allowed to cure to a film thickness having the desired  
properties. The pigments can be introduced into the coating by  
first forming a mill base with the polyester polyol. The mill  
base can be formed, for example, by conventional sand-grinding  
15 or ball-milling techniques, and then blended, by simple  
stirring or agitation with the other ingredients of the  
composition.

The combination of the molybdate-modified zinc  
phosphates, the zinc salts of benzoic acid, e.g. zinc benzoate  
20 and an alkaline earth metal phosphate, e.g., zinc or zinc-  
barium phosphates, improved the corrosion resistance while  
maintaining all the other desirable characteristics required of  
the coating. In other words, the specific combination of a  
zinc molybdate-zinc phosphate, a zinc salt of substituted  
benzoic acid and zinc or zinc-barium phosphates, in the ratios

1 stated, improved the corrosion inhibition substantially when  
compared to the use of either one of these metal salts alone in  
the same coating.

5 More specifically in preparing the urethane resins, the  
preferred polyester polyols of this invention have equivalent  
weights ranging from about 260 to 970 with hydroxyl numbers  
ranging from 40 to 252 and an acid number less than 10. The  
polyols includes a variety of polyester polyhydroxyl compounds  
known in the art including, for example, the condensation-  
10 reaction products of pentaerythritol and/or glycols with  
monocarboxylic acids or an aromatic or aliphatic dicarboxylic  
acid. Any branched-chain glycol maybe used in the formation of  
the polyester, although it is preferred that these glycols  
contain no more than 8 carbon atoms. A useful polyol is formed  
15 where the molar ratio of glycol to pentaerythritol is from 2:1  
to about 6:1. The carboxylic acid component of the polyester  
polyol prevents the molecular weight build-up of the polyol.  
It has been found that any aromatic or aliphatic monocarboxylic  
acid or mixtures of these having 18 or less carbon atoms can be  
20 used. Normally, the acids are used in a molar ratio of acid to  
polyalcohol of about 1:1 to 2.5:1.

25 Examples of aromatic monocarboxylic acids include benzoic  
acid, butylbenzoic acid, triethyl benzoic acid, toluic acid,  
phenylacetic acid, and the like. Examples of aliphatic acids  
are acetic acid, propionic acid, butyric acid, valeric acid,

1 caproic acid, caprylic acid, pelargonic acid, capric acid,  
lauric acid, myristic acid, palmitic acid, stearic acid, etc.

The dicarboxylic acids useful in the formation of the polyester polyols have the general formula:



where R is aliphatic or aromatic group. Preferred are succinic acid, glutaric acid, adipic acid and pimelic acid. Useful acids are those in which R has 2 to 8 carbon atoms with the preferred being maleic acid and itaconic acid. The aromatic  
10 dibasic acids are phthalic, isophthalic, and terephthalic, although other aromatic dibasic acids can be used.

It is known that the lower alkyl mono- or diesters of these acids and the anhydrides thereof can be used in place of the free acids. Other known polyester polyols can be obtained  
15 by the condensation reaction between a polybasic acid, such as adipic acid, phthalic anhydride, isophthalic acid, etc., and a diol or triol, such as ethylene glycol, diethylene glycol, propylene glycol, trimethylol propane, glycerine, etc.

The hydroxyl numbers of the preferred polyester polyols  
20 should be at least 40 and preferably between 40 and 252. The polyesters, containing hydroxyl groups, are combined with the polyisocyanate. This combination can be carried out in several ways known to the art. For example, an organic solution of the

1 polyester containing, if desired, a catalyst-promoting urethane  
formation such as an organo-tin compound, is added to an  
chemical equivalent amount of the isocyanate. The combination  
is made at ambient temperature but the heat of reaction usually  
5 causes an increase in temperature. The mixture is agitated  
preferably at room temperature until the urethane reaction is  
substantially completed. The course of the reaction can be  
followed by noting the viscosity of the mixture. When the  
viscosity becomes substantially constant, it may be concluded  
10 that the reaction is substantially completed. The resultant  
reaction product may contain insignificant amounts of free  
isocyanate and/or hydroxyl groups.

Alternatively, the polyester solution can be reacted with  
a small excess, e.g. about 10% excess of the isocyanate. After  
15 the urethane reaction is substantially completed, the excess  
NCO groups can be reacted with "chain-extending" substances,  
e.g. water, alcohols, etc. This procedure results in polymers  
of substantially equivalent character but permits the reaction  
to proceed at a faster rate, due to the mass action of the  
20 excess NCO groups. The term "small excess" is intended to be  
included within the meaning of the term "stoichiometric  
amounts".

The polyisocyanates and particularly the aliphatic  
polyisocyanates based on HDI include various multi-functional  
25 aliphatic polyisocyanates having an isocyanate content (NCO)

1 ranging from about 10 to 30% by weight with an equivalent  
weight (NCO) ranging up to about 300. Specific examples of the  
organic polyisocyanates used in this invention make up about 5  
to 30% and preferably 5 to 20% by weight of the film-forming  
5 blend. These compounds include aliphatic, cycloaliphatic,  
alkaryl, aralkyl, heterocyclic, and aryl di- or triisocyanates.  
Specific compounds include, for example, polyisocyanates such  
as:

diphenylmethane-4,4'-diisocyanate,

10 diphenylene-4,4'-diisocyanate

toluene-2,4-diisocyanate,

toluene-2,6-diisocyanate,

3,3'-dimethoxy-4,4'-diphenylene diisocyanate methylene-  
bis-(4-cyclohexyl isocyanate)

15 tetramethylene diisocyanate,

hexamethylene diisocyanate,

decamethylene diisocyanate,

ethylene diisocyanate,

ethylidene diisocyanate,

20 propylene-1,2-diisocyanate,

cyclohexylene-1,2-diisocyanate,

m-phenylene diisocyanate,

p-phenylene diisocyanate, 1,5-naphthalene diisocyanate,

3,3'-dimethyl-4,4'-biphenylene diisocyanate,

25 3,3'-dimethoxy-4,4'-biphenylene diisocyanate,

3,3'-diphenyl-4,4'-biphenylene diisocyanate,

1 4,4'-biphenylene diisocyanate,  
3,3'-dichloro-4,4'-biphenylene diisocyanate,  
furfurylidene diisocyanate,  
bis-(2-isocyanatoethyl)fumarate,  
5 1,3,5-benzene triisocyanate,  
para, para', para"-triphenylmethane triisocyanate,  
3,3'-diisocyanatodipropyl ether,  
xylylene diisocyanate,  
B,B-diphenyl propane-4,4'-diisocyanate, and  
10 isophorone diisocyanate. Preferred polyisocyanates include  
hexamethylene diisocyanate and methylene-bis-(4-cyclohexyl  
isocyanate) e.g. DESMODUR-N.

By selecting the proper polyols and by adjusting the NCO  
to OH ratio, the physical properties and efficiency of the  
15 film, such as the strength of film, flexibility, chemical  
resistance, solvent resistance, etc., can be controlled over a  
wide range. Compounds where the NCO to OH ratio ranges from  
0.85 to 1.4 of NCO to 1.0 of OH groups e.g. 1.2:1 are useful  
for the manufacture of coating in accordance with this  
20 invention.

If the coating is derived from a two-package system, the  
polyisocyanate is in one package and a solution of the polyol  
is in a separate package. The two reactants, one containing  
the pigments, are thoroughly mixed just before applying the  
25 coating onto the surface. Separation of the two reactants is

1 usually necessary since the "pot life" of some of the  
compositions is short. The polyisocyanate (NCO) reacts with  
the hydroxyl groups of the polyol at temperature as low as  
about 40°F (4°C). Regardless of the method by which the  
5 coating composition is prepared, the coating should contain 20  
to 60 parts by weight of the polyurethane resin and up to about  
50 parts, e.g. 0-50 parts by weight of solvent. The solvent of  
the composition can be a mixture of organic solvents wherein  
the constituents of the urethane react.

10 Instead of the two-component or "two-package" system, a  
"one package" coating can be used if the reactive groups of the  
polyisocyanate are blocked with a blocking agent such a  
methylethyl ketoxime. This eliminates the need for keeping the  
polyol apart from the polyisocyanate until just before use.  
15 When the coating, with the blocked polyisocyanate, is applied  
and heated the blocking agent is released, permitting the  
polyisocyanate to react with the polyester polyol.

The blocking agents are used for purposes of masking the  
free isocyanate radical of the polyisocyanates. These agents  
20 include phenol, m-nitrophenol, p-chlorophenol, ethyl malonate,  
acetylacetone, ethyl acetoacetate, cresol, methanol, ethanol,  
ethylene, chlorophydrin, etc. Although the temperatures at  
which the above-mentioned blocking agents are dissociated  
varies with the agents, it is generally accepted that heating  
25 is required to deblock.

1           The coating composition also can contain ultraviolet  
light stabilizers, antioxidants, catalysts, wetting or  
dispersing agents, e.g., Anti-Terra-204 (carboxylic acid salts  
of polyamine-amides), flow modifiers e.g. BYK-320 (polyether  
5 modified methylalkyl polysiloxane copolymers), adhesion  
promoters, etc. The ultraviolet light stabilizer can be  
present in an amount of 1-10% by weight, based on the weight of  
the urethane binder. The antioxidants can be present also in  
amounts of 0.1-3% by weight of the urethane binder.  
10 Ultraviolet light stabilizers include benzophenones, triazoles,  
triazines, benzoates, substituted benzenes, organophosphorous  
sulfides, etc.

          The coating composition of this invention may contain  
about 0.01-2.0% by weight, based on the weight of the polymer  
15 forming blend, of a curing catalyst. The catalysts are usually  
organo metallics such as dibutyl tin dilaurate and zinc  
octoate, dibutyl tin di-2-ethylhexoate, stannous octoate,  
stannous oleate, zinc naphthenate, vanadium acetyl acetate,  
and zirconium acetyl acetate. Also useful as catalysts are  
20 tertiary amines, such as, for example, triethylene diamine,  
triethylamine, pyridine, dimethylaniline, and methyl  
morpholine. When a two-component system is used, the catalyst  
can be added to either the polyisocyanate or the solution of  
the polyester polyol.

1           The coating composition of this invention can be applied  
to a variety of substrates by conventional application methods  
such a spraying, dipping, brushing, or flow coating.  
Substrates that can be coated with the composition are, for  
5       example, metal, wood, glass, or plastics such as polypropylene,  
polystyrene, and the like. The coating is particularly suited  
for application over pretreated or unprimed metal. The coating  
can be cured at ambient temperatures or heated at 40°-120°C.  
for up to an hour or more. If the coating contains a blocked  
10       polyisocyanate, temperatures ranging up to about 160°C may be  
necessary.

          The solvent may include a mixture of organic solvents,  
e.g., benzene, toluene, xylene, and naphtha. Ester solvents  
include the acetates, e.g., ethyl acetate, butyl acetate, hexyl  
15       acetate, amyl acetate, etc., propionates such as ethyl  
propionate, butyl propionate, etc. Ketone solvents include  
acetone, methyl-ethyl ketone, methyl-isopropyl ketone, methyl-  
isobutyl ketone, diethyl ketone, cyclohexanone, etc. Glycol  
ester solvents include ethylene glycol, monoethyl-ether  
20       acetate, etc.

          In testing the coatings prepared in accordance with this  
invention, the corrosion protection for an aluminum substrate  
was found to be over 2000 hours in 5% salt spray in accordance  
with ASTM Test Method B-117 and over 500 hours in SO<sub>2</sub>/salt  
25       spray in accordance with ASTM Test Method G-85. The coating

1 was found to have outstanding performance when exposed to  
extreme heat conditions, high intensity of light and water,  
extreme cold conditions, hot lubricating oils and other  
chemicals normally found in aircraft operations. By utilizing  
5 the coating composition of this invention, a corrosion  
resistant film can be obtained on various substrates. The  
coating therefore has properties which function as a primer and  
more important as a single topcoat which is highly adherent,  
flexible, chemical resistant and resistant to all weather  
10 conditions. The coatings of this invention lower the risk of  
failure due to cracking especially at low temperatures and are  
easily touched-up since only one coating need be applied.  
Since the coating requires only one coat, it requires less time  
for application and removal and thereby saves on manpower that  
15 would generally be needed in the preparation of a two coat  
system. Moreover, the present coating provides protection at  
lower film thicknesses thereby reducing the weight of the  
coating compared to a two-coat paint system which is an  
important factor when considering aircraft coatings.

20 It is obvious that there are other variations and  
modifications which can be made with respect to this invention  
without departing from the spirit and scope of the invention

ABSTRACT OF THE DISCLOSURE

A corrosion-resistant coating which can be applied directly to a surface as a self-priming topcoat comprising a polyurethane resin binder and a combination of pigments consisting essentially of a molybdate-modified zinc phosphate, zinc salts of benzoic acids, and an alkaline earth metal phosphate such as zinc-barium phosphate. In addition, the coating contains up to about 35 parts by weight of a titanium dioxide pigment, up to about 3.0 parts by weight of an oil soluble dispersant agent and up to about 50 parts by weight of at least one organic solvent.